



Shell Chemicals

The Development and Commercialization of Biodegradable Selectively Branched Detergent Alcohols

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Surfactants

Multi-million ton/ year global business

Anionic surfactants are the largest group

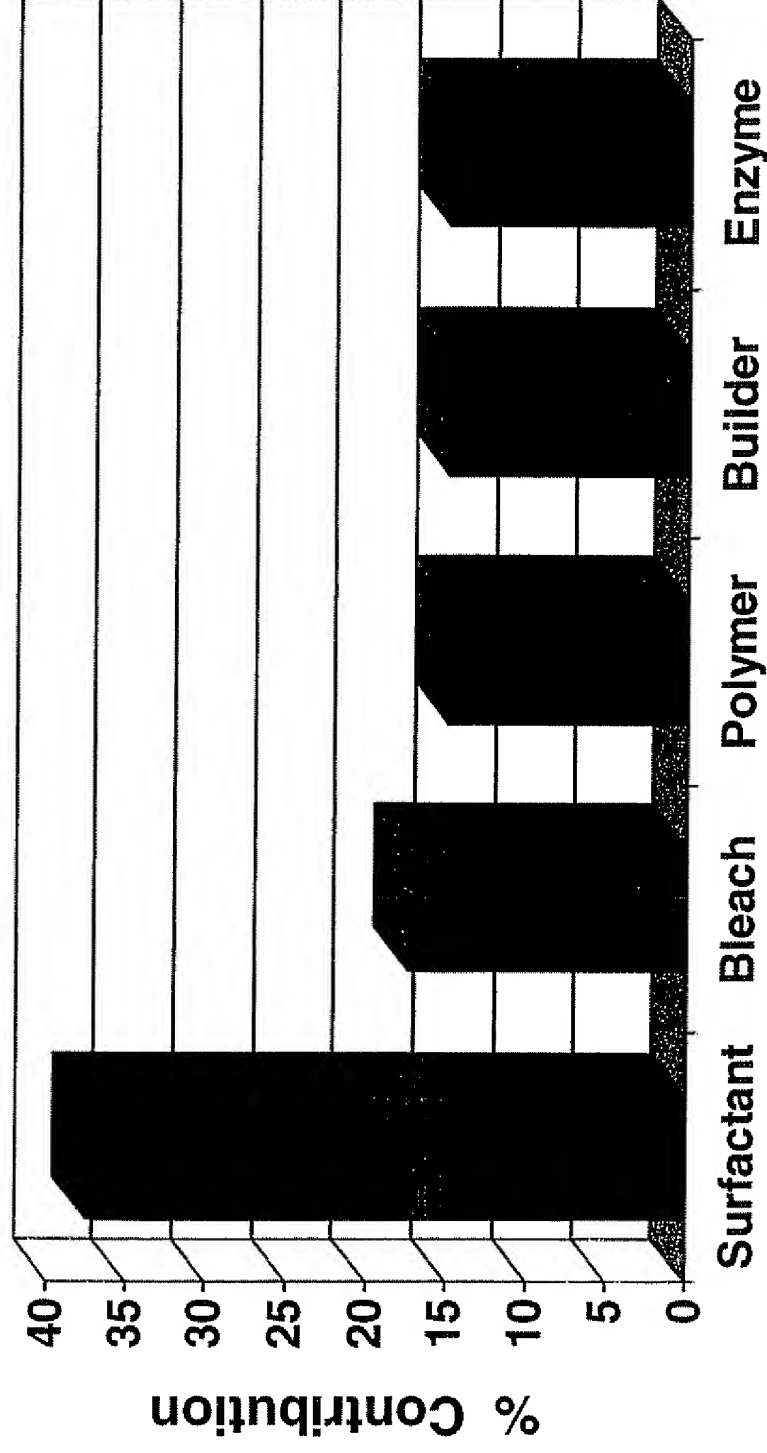
They wet fabrics and soils; remove dirt and stains

The single most important cleaning ingredient in most laundry and household cleaning products



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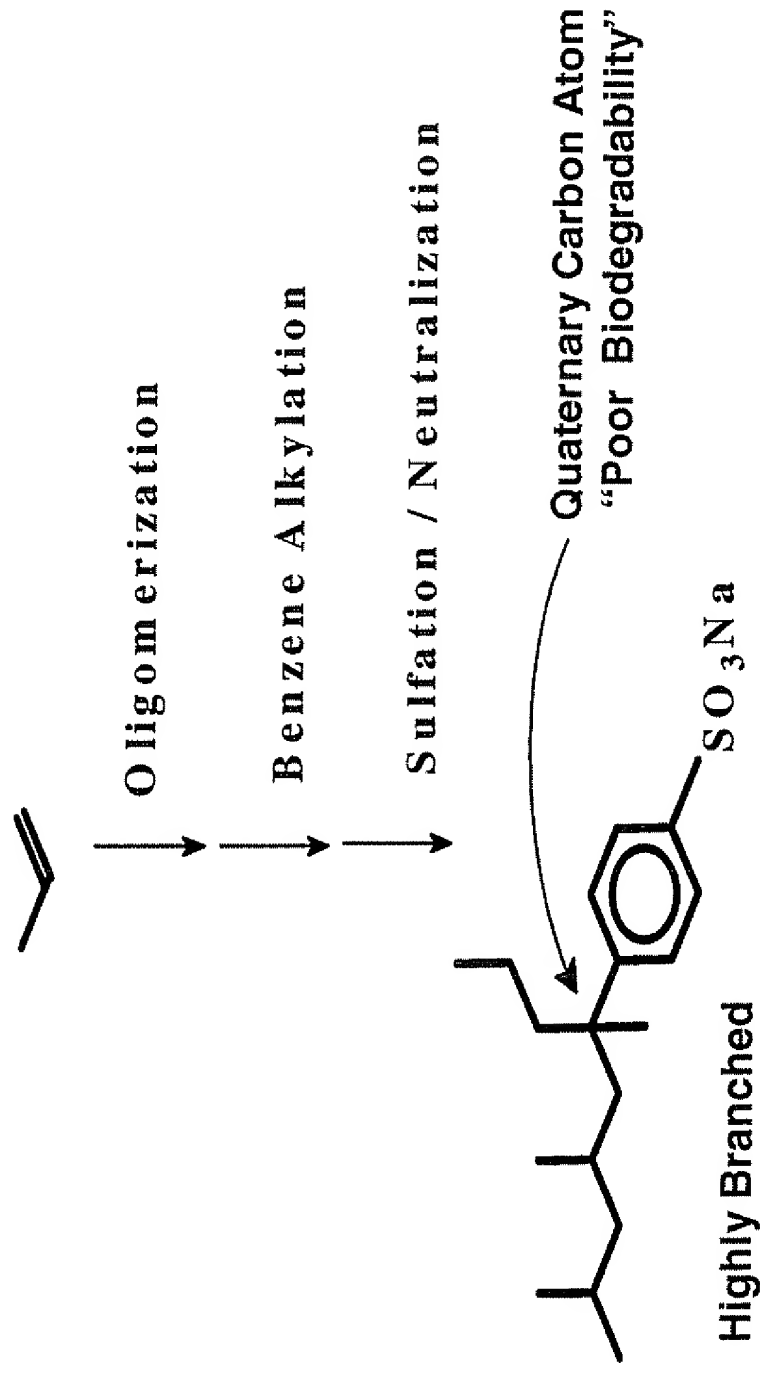
Performance Contribution to Detergency



* G. Baillely et al., *Proceedings of the 5th World Conference on Detergents*, (2003)



1950's Vintage Alkylbenzene Sulfonate



Highly Branched

Quaternary Carbon Atom “Poor Biodegradability”



Surfactant Events – A Need for Innovation

1950's - Highly Branched Alkylbenzene Sulfonates, (ABS)
slow biodegradation, foaming, aquatic toxicity?

1960's – ABS Regulation begins – Rapid replacement by
Biodegradable Linear Alkylbenzene Sulfonates,
Linear Alcohol Sulfates and Linear AES

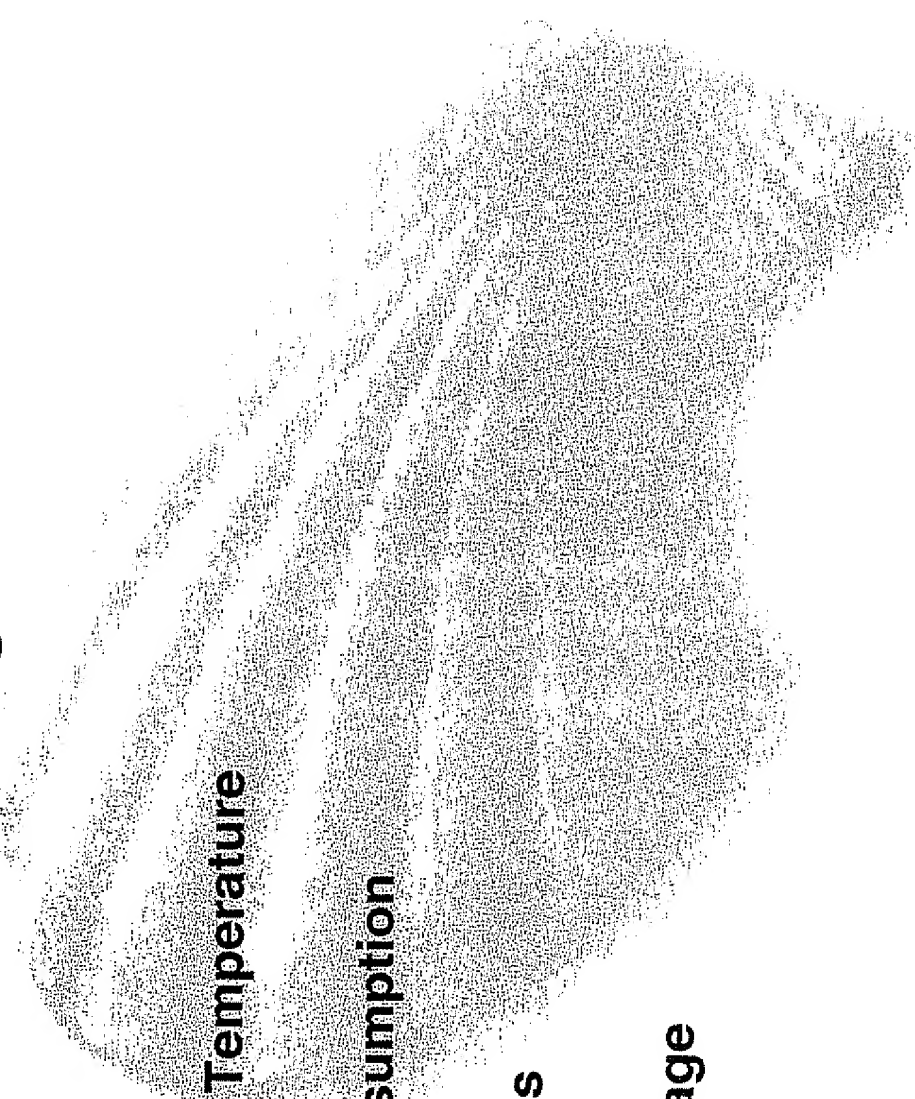
A Paradigm is born: “*Alkyl branching is Bad*”

1970's - Movement to lower wash temperatures creates a
need for better cold water detergency

1980's *The Alkyl Branching Paradigm is Challenged*

2000's - High Solubility Biodegradable, Selectively
Branched Detergents are commercialized

Recent Trends in Washing Processes

- 
- Lower Wash Water Temperature
 - Lower Energy Consumption
 - Shorter Wash Times
 - Reduced Water Usage



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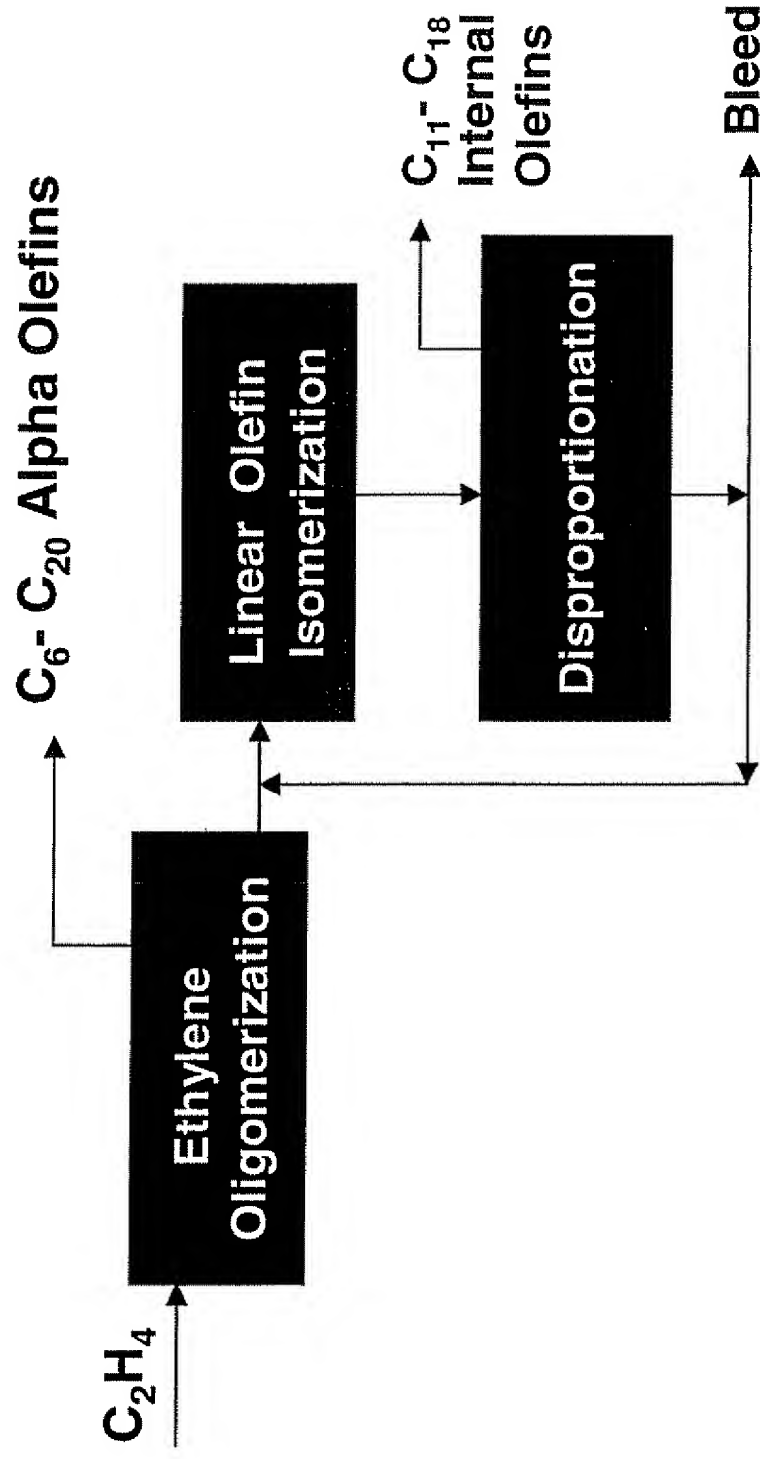
Desired Surfactant Properties

- Excellent Surface Activity
- Readily Biodegradable
- Superior Cold Water Detergency
- Improved Hard Water Solubility
- Ability to use Less Surfactant
- Affordable and Consistent Production



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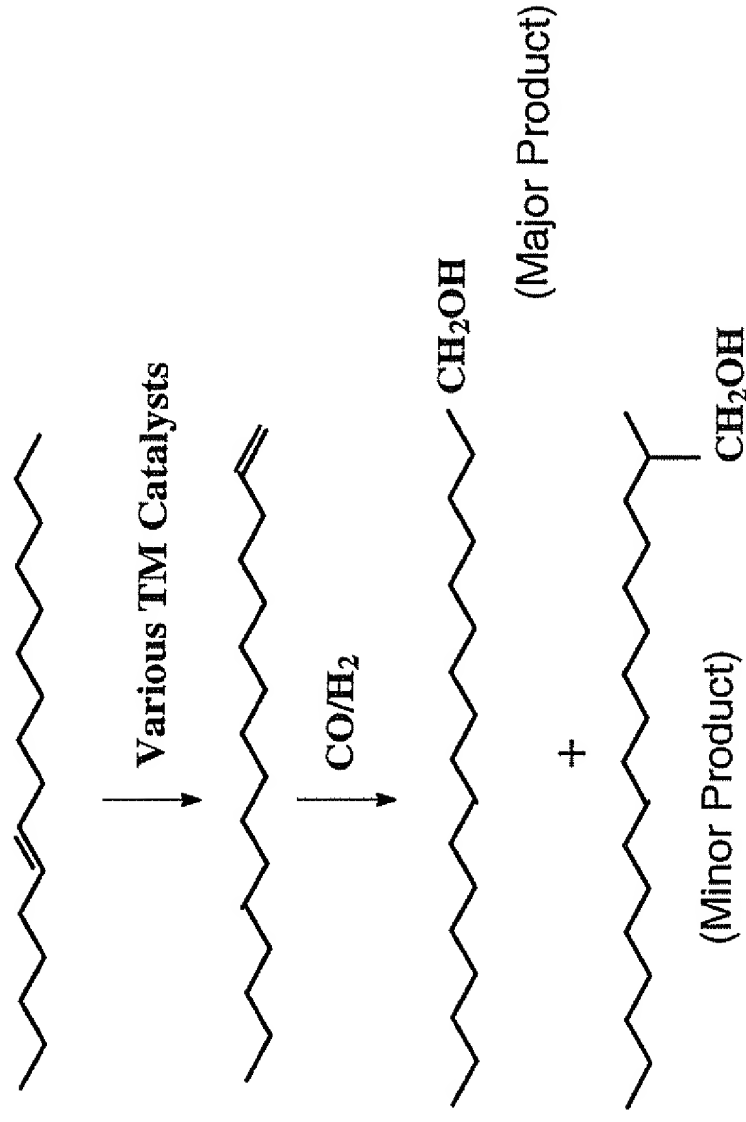
Shell Higher Olefins Process (SHOP)





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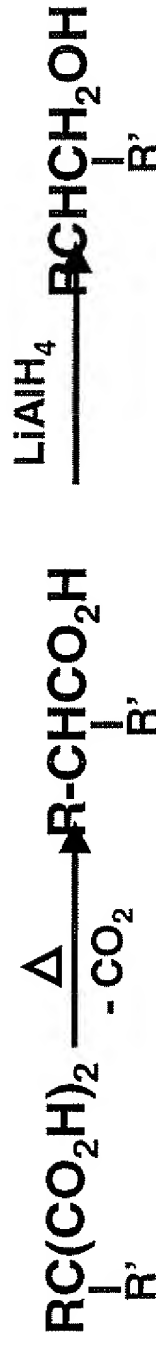
Shell Hydroformylation Process (SHF)





Model Compound Studies

Malonic Ester Synthesis of 2-Alkyl Branched Alcohols



Alcohols were converted to the alcohol sulfate sodium salts by treatment with ClSO_3H , followed by neutralization with NaOH



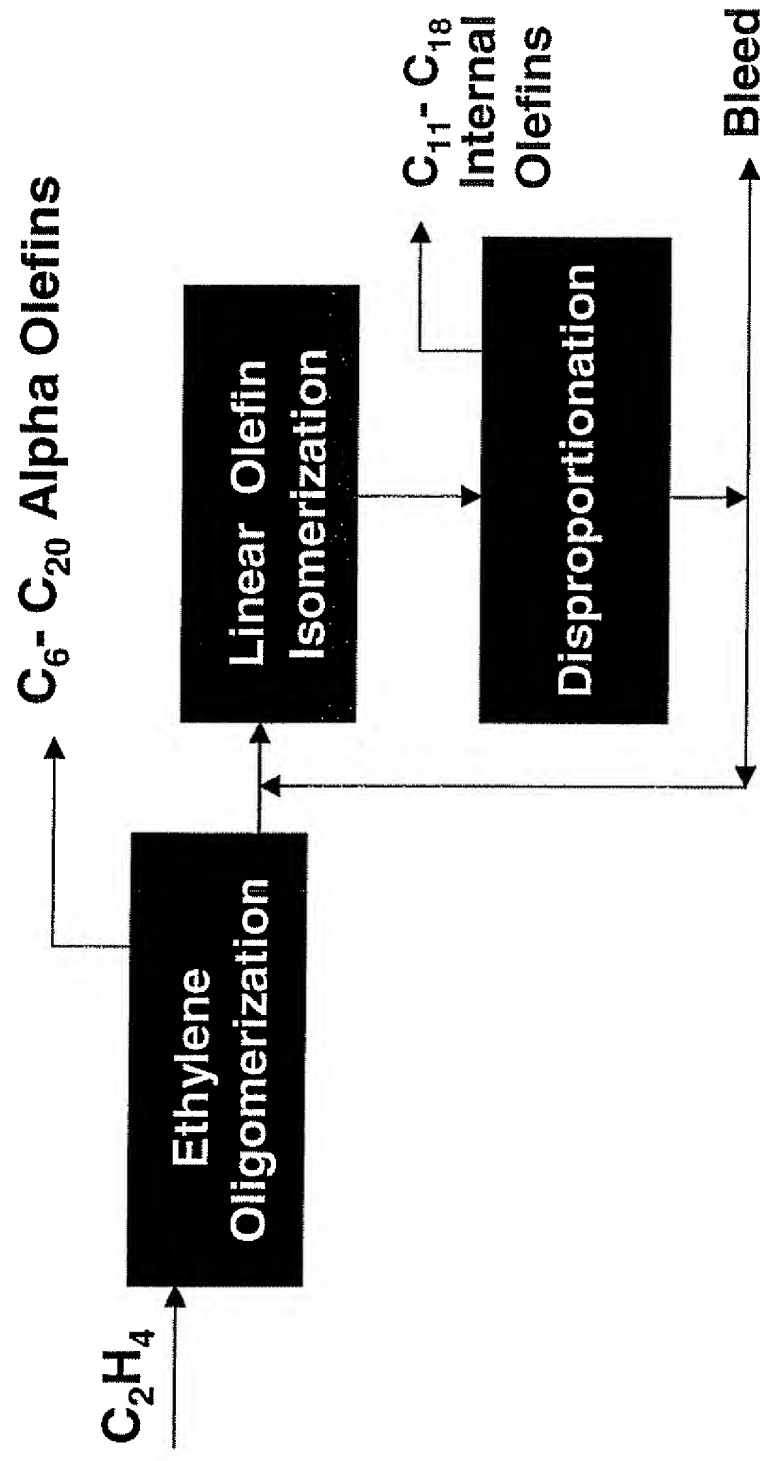
How to Introduce Controlled Branching

- **Controlled Dimerization / Oligomerization of Lower Olefins**
- **Cross Metathesis Schemes**
- **Selective Skeletal Isomerization of Linear Olefins**
 - Use a proprietary, “pore engineered” zeolite catalyst
 - Makes mainly mono-branched olefins with the alkyl groups distributed at beneficial positions along the backbone
- Very low level of quaternary carbon atoms in product



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Shell Higher Olefins Process (SHOP)

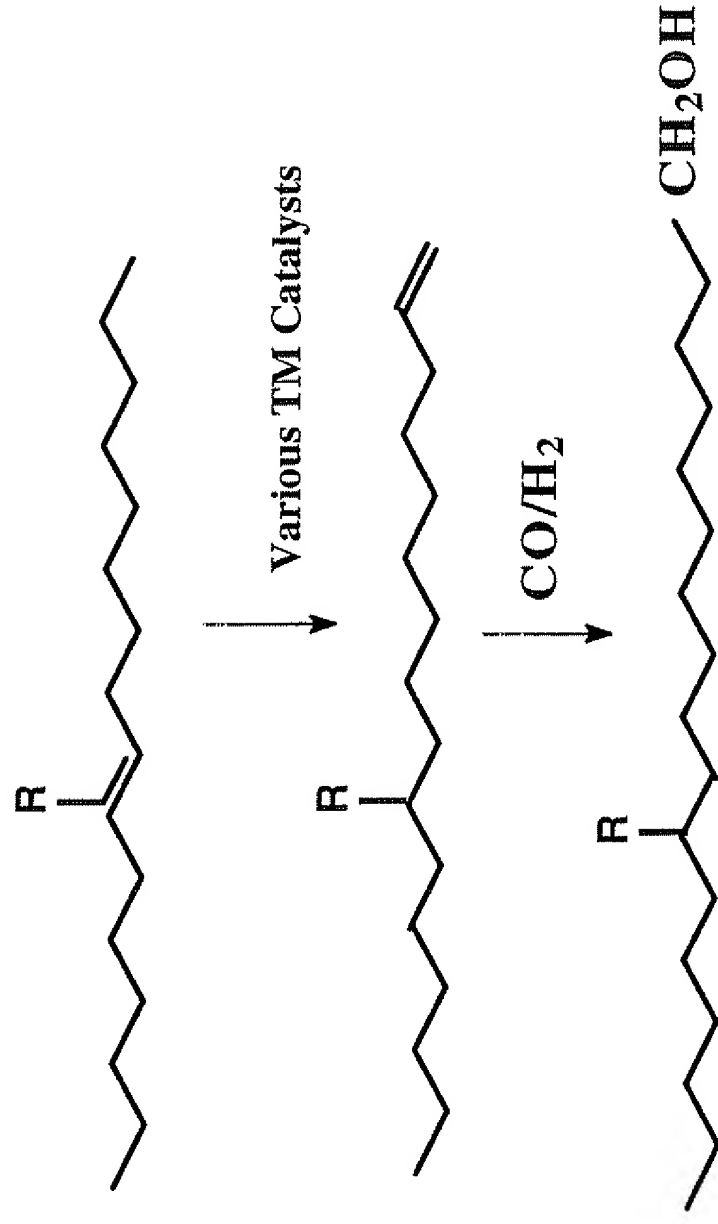




Skeletal Olefin Isomerization Process

- **Uses Alpha or Internal Olefins as Feedstocks**
- **Low Severity Operation**
- **Thermodynamic Equilibrium Conversion (>95%)**
- **Very High Selectivity (>98%)**
- **Multiply Regenerable Zeolite Catalyst**
- **Fully Compatible with the SHOP and SHF Processes**
- **Very High Catalyst Turnover Rate**

Shell Hydroformylation Process

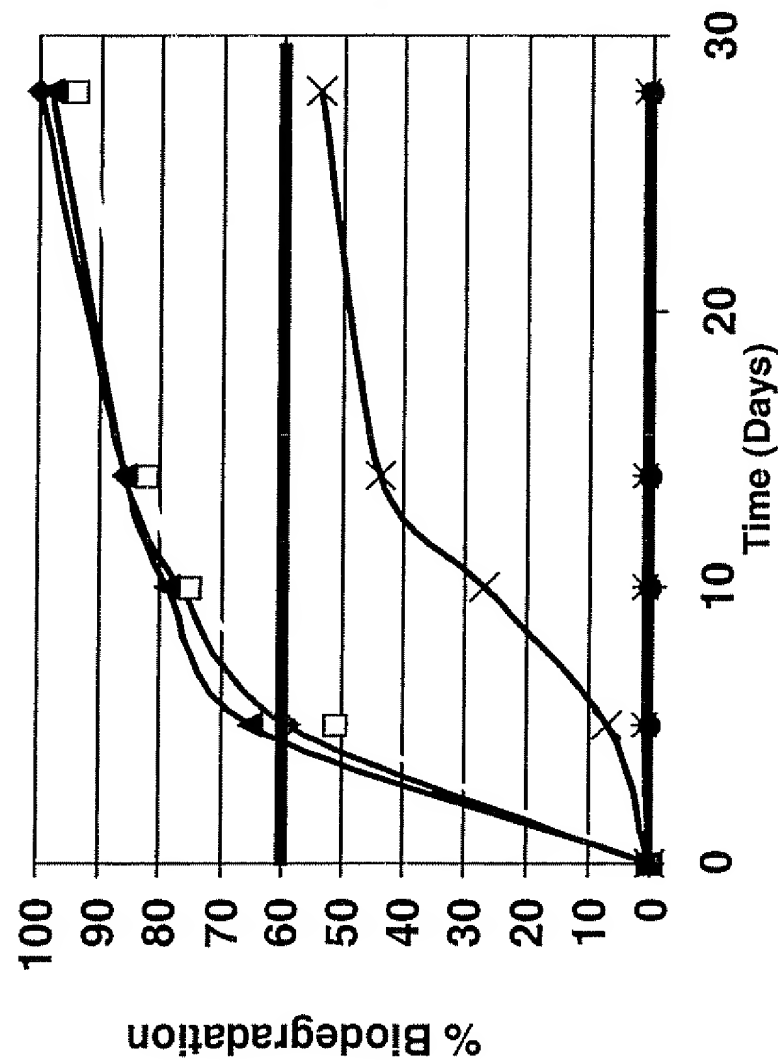


R distributed at desirable positions along backbone



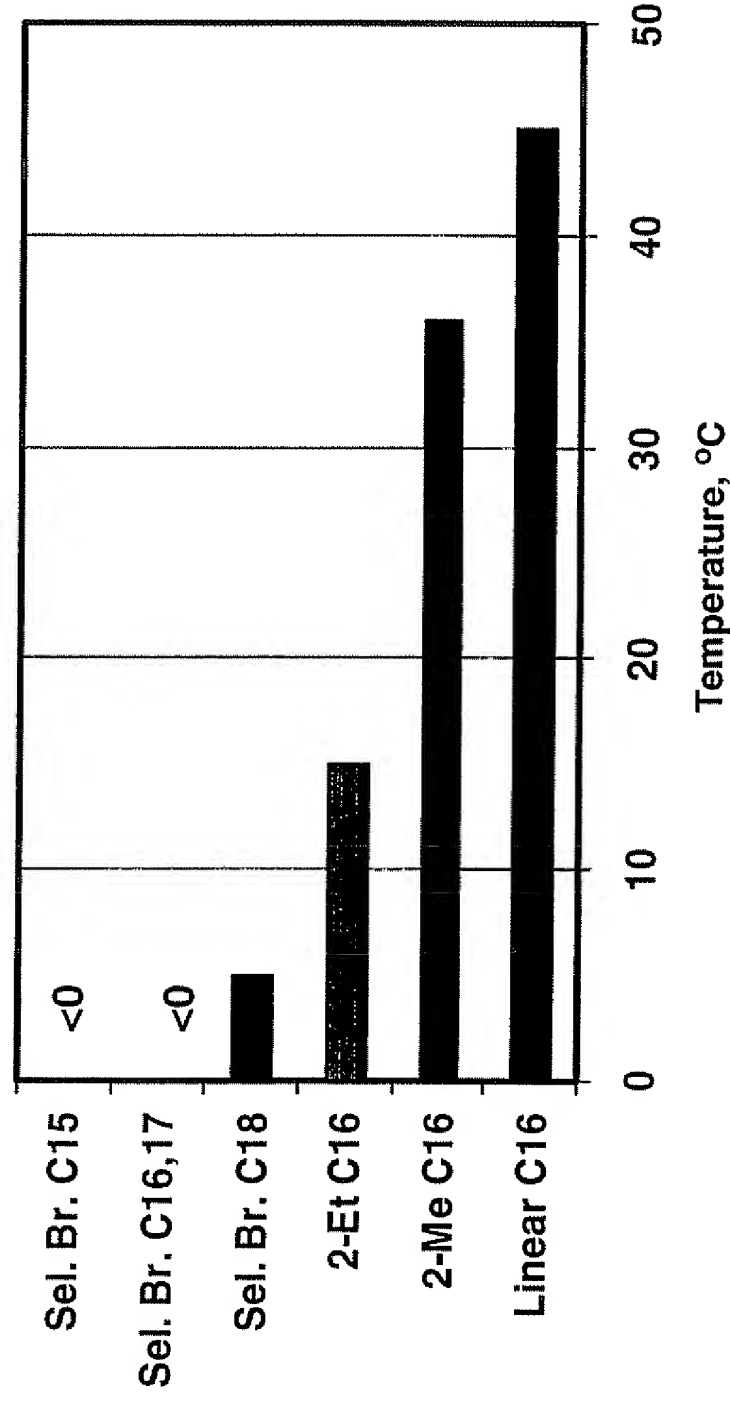
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Closed Bottle Biodegradation Results for Various Alkyl Alcohol Sulfates

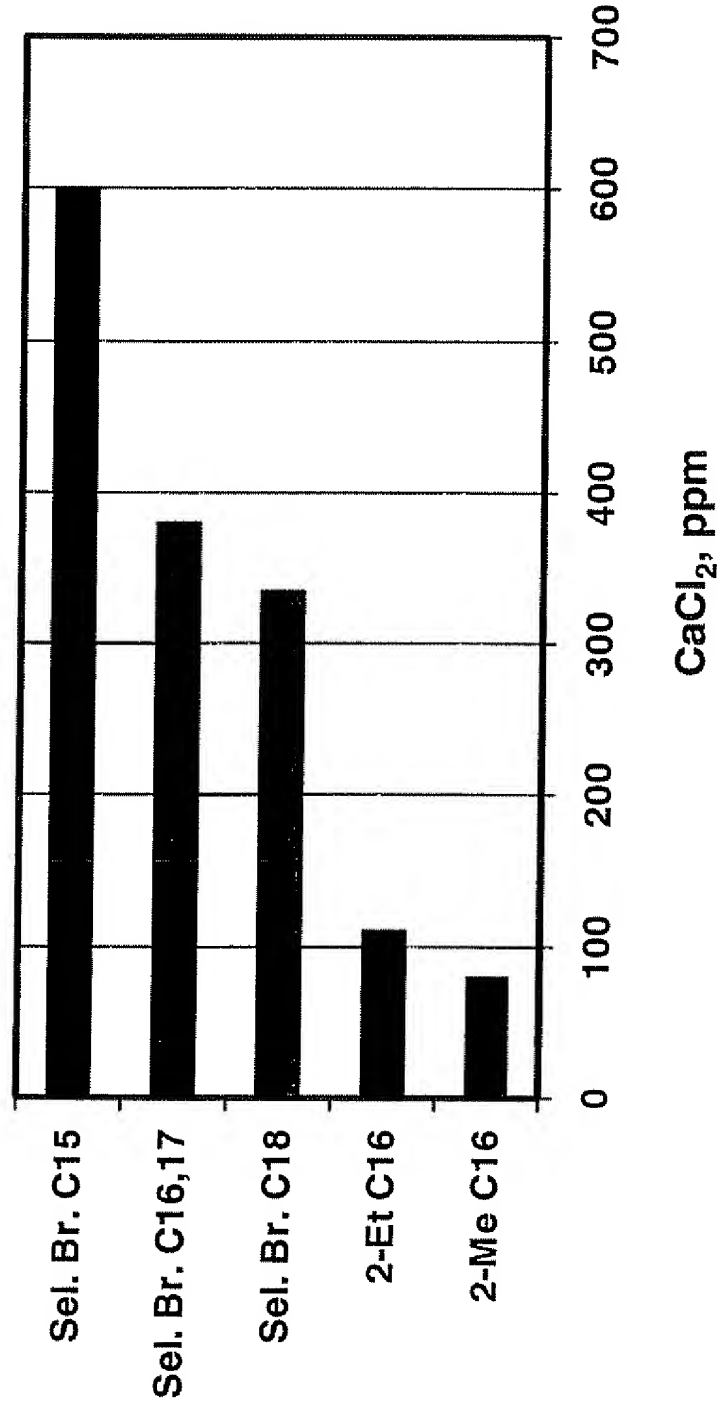


◆ Sel.BrC14,15 AS
□ 2-alkyl C14,15 AS
▲ Linear C14,15 AS
× HB Propylene Tetramer C13 AS
* Quat C9 AS
● Quat C15 AS

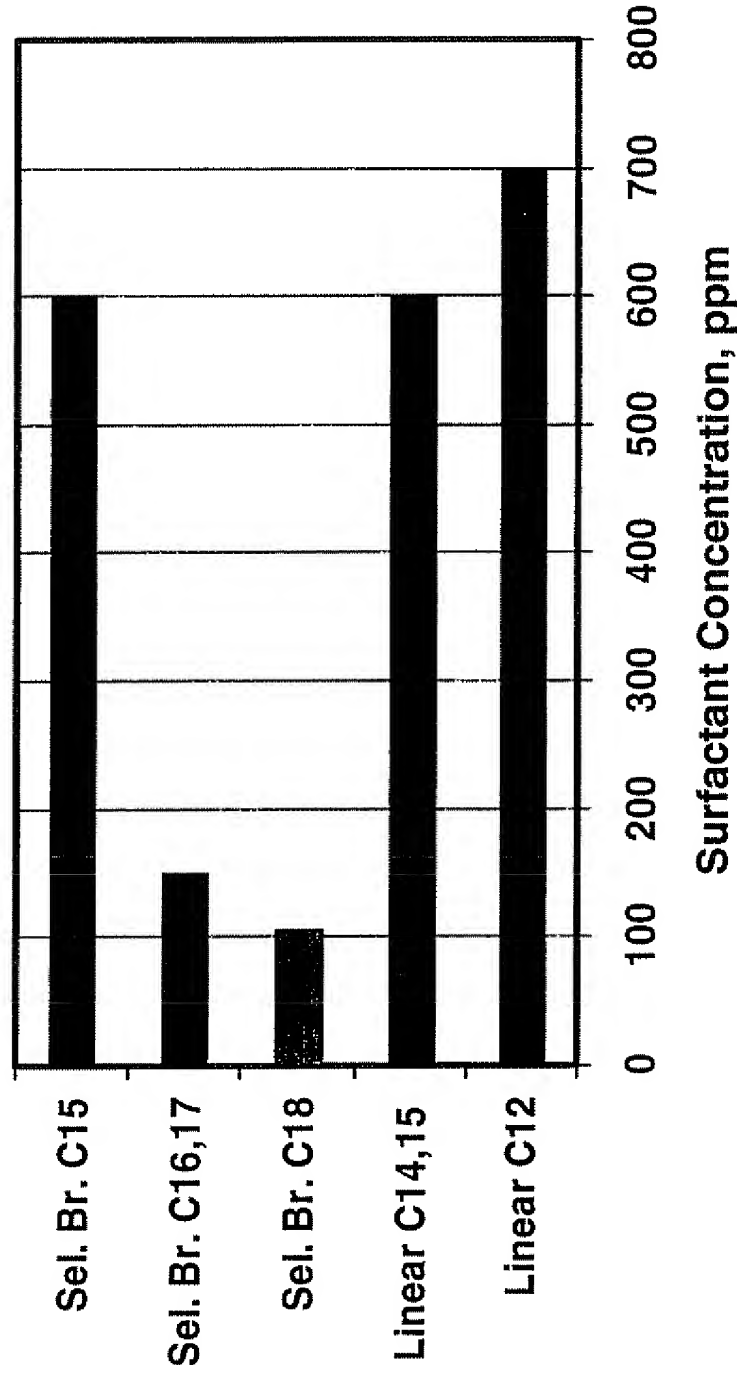
Krafft Temperature of the new Selectively Branched Alcohol Sulfates



Calcium Tolerance of the new Selectively Branched Alcohol Sulfates



Critical Micelle Concentration of the Selectively Branched Alcohol Sulfates

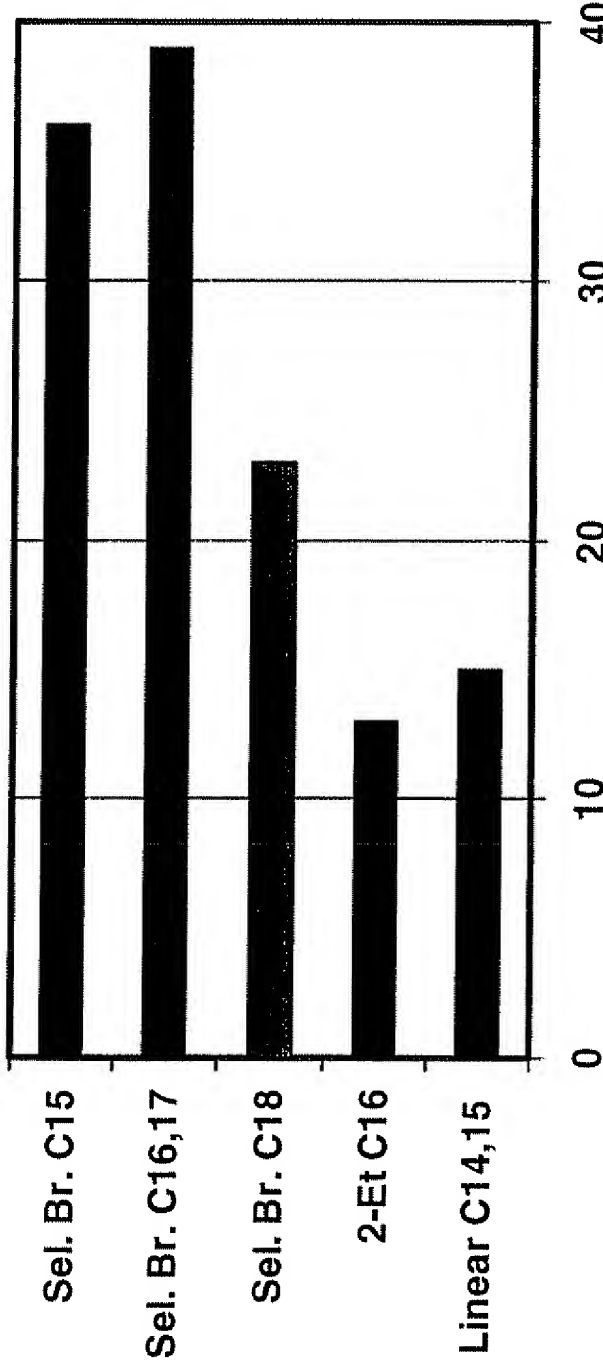




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Detergency Performance of the new Selectively Branched Alcohol Sulfates

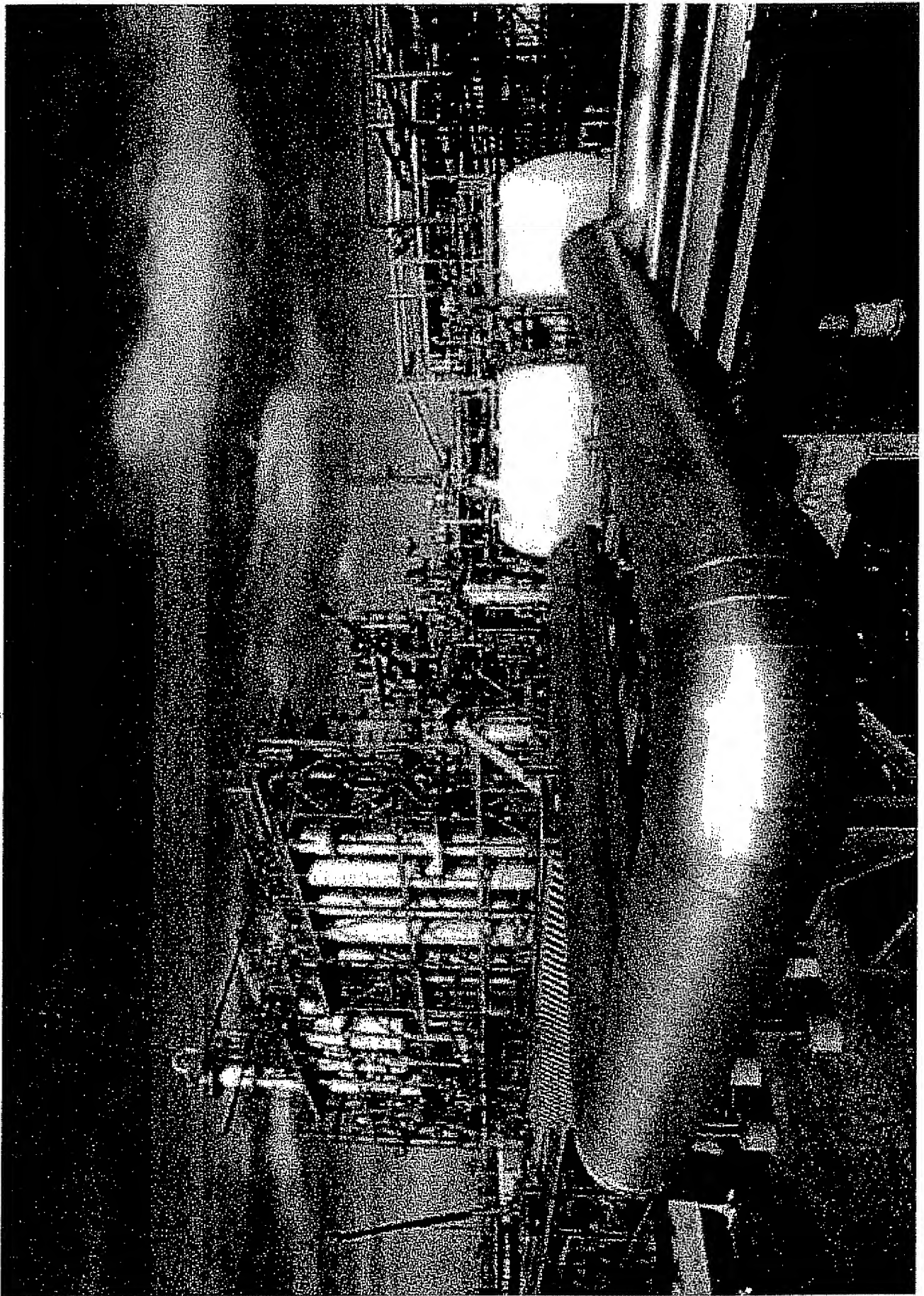
(at 10°C and 150 ppm Water Hardness)



% Soil Removal, $LSD_{95} = 4$

Partnering with Procter & Gamble

- P&G is a **Leading Global Supplier** to the Detergent Industry
- P&G conducted independent studies that pointed to a Primary Alcohol with a single methyl branch near the middle of the chain
- Evaluated various Shell “Selectively Branched” Alcohols
- Derivatized and formulated products based on the new alcohols
- A joint decision was made to commercialize the Innovation





Commercialization

- Product was scaled up in several stages (6, 50 and 3700 tonnes)
 - Allowed Process Modeling and Design Optimization
 - Customer feedback
- P&G worked closely with Shell during the Process
 - HS&E Studies, Alcohol Conversion and Product Formulation
 - Logistics, Product Specifications
 - Market Development Work
- World-Scale Olefin/Alcohol Plant built at Geismar, LA. in 2001
 - On spec product produced within 12 hours of feed-in
 - Breakthrough Technology Confirmed in Operations
- Alcohols successfully formulated into Quick Dissolving Tide®

“Tide is the most popular laundry detergent used in the USA”



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New Opportunities

▪ Personal Skin Care Products

- Excellent Emollient / Moisturizer
- Non-oily
- Good Viscosity and Solubility Characteristics
- Biodegradable

▪ Industrial Fluids

- Low Pour Point
- Good Stability

▪ Chemical Intermediates

- Novel Composition
- Reagent for Various Industries

Acknowledgements

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